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10th Internat'l IUPAC Conference on High Temperature Materials Chemistry **(Statement A)**
(Juelich, Germany, 10-14 April 2000) (Deadline: 31 March 2000)
and Seminars at Max Planck Inst., Univ of Dortmund, Univ. of Basel, Apr 4, 7, 18

Matrix Isolation of Boron and Carbon Vapor.
Control of Cluster Formation During Preparation and Annealing.

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Universität Dortmund
Fachbereich Chemie
Anorganische Chemie
Dortmund, Germany
18 April 2000

Kinetics of formation of cyclic C_6 and cyclic C_8 and of B_JC_{n-J} clusters (J = 0, 1, 2; n = 3-11) in solid argon

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Institute für Physikalische Chemie
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Basel, Switzerland
7 April 2000

Kinetics of formation of cyclic C_6 and cyclic C_8 and of B_JC_{n-J} clusters (J = 0, 1, 2; n = 3-11) in solid argon

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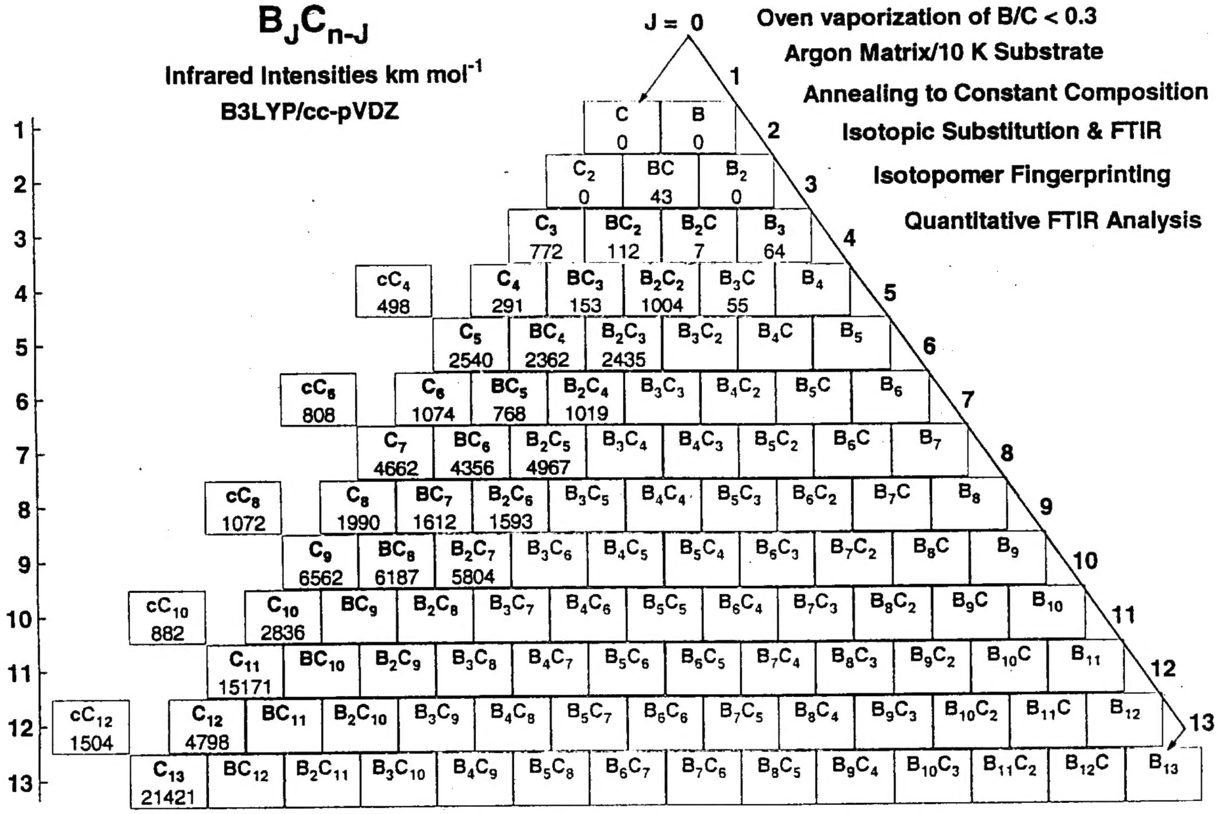
Max Planck Institute für Kernphysik
Heidelberg, Germany
5 April 2000

GOAL - 5% atoms in matrix



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Goal

Production of cryogenic HEDM with five mole percent atoms.

Objective

Characterization of source and quantitative analysis of B_JC_{n-J}

Approach

Production of HEDM by evaporation of boron with high-temperature graphite furnace and co-deposition of vapor with argon on a cold (10 K) surface

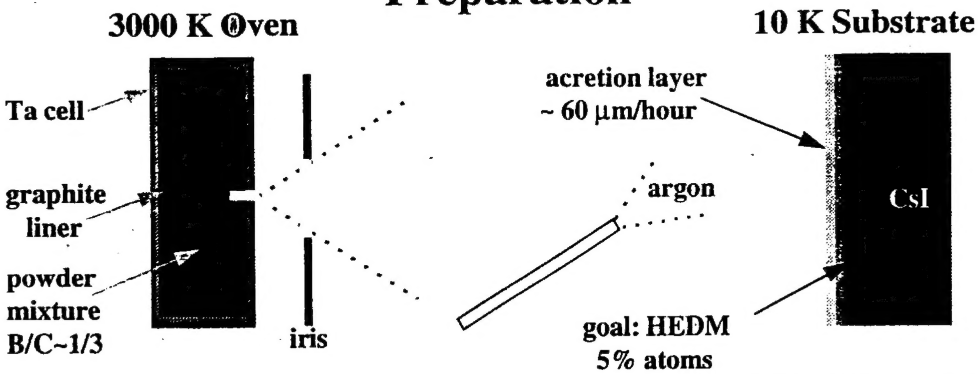
Identification and quantitative analysis of B_JC_{n-J} species ($n \geq 3$, $J = 0$ to 2) by FTIR spectroscopy and *ab-initio* calculations.

Quantitative measurement of distributions of B_JC_{n-J} species produced upon deposition and after annealing to a constant composition.

Determine absolute column densities (molecules cm^{-2}) from Beer's law:

$$<\rho_i l> = 2.303\, A_{exp}/I_{theory}$$

Preparation

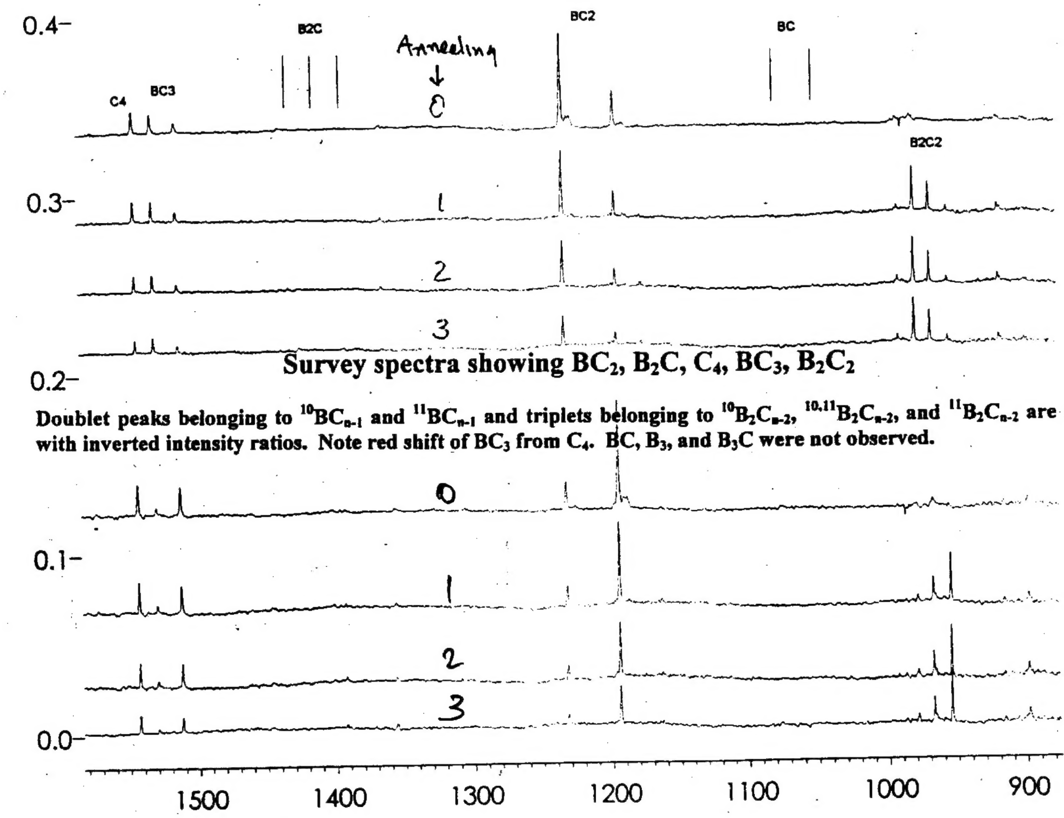


Annealing

a0 10 K	a3 32.5 K, 60 s	a6 40.0 K, 20 s
a1 27.5 K, 120 s	a4 35.0 K, 45 s	sublimation
a2 30.0 K, 90 s	a5 37.5 K, 20 s	rate ~ 1 μm/s

Precision matched pair of matrices

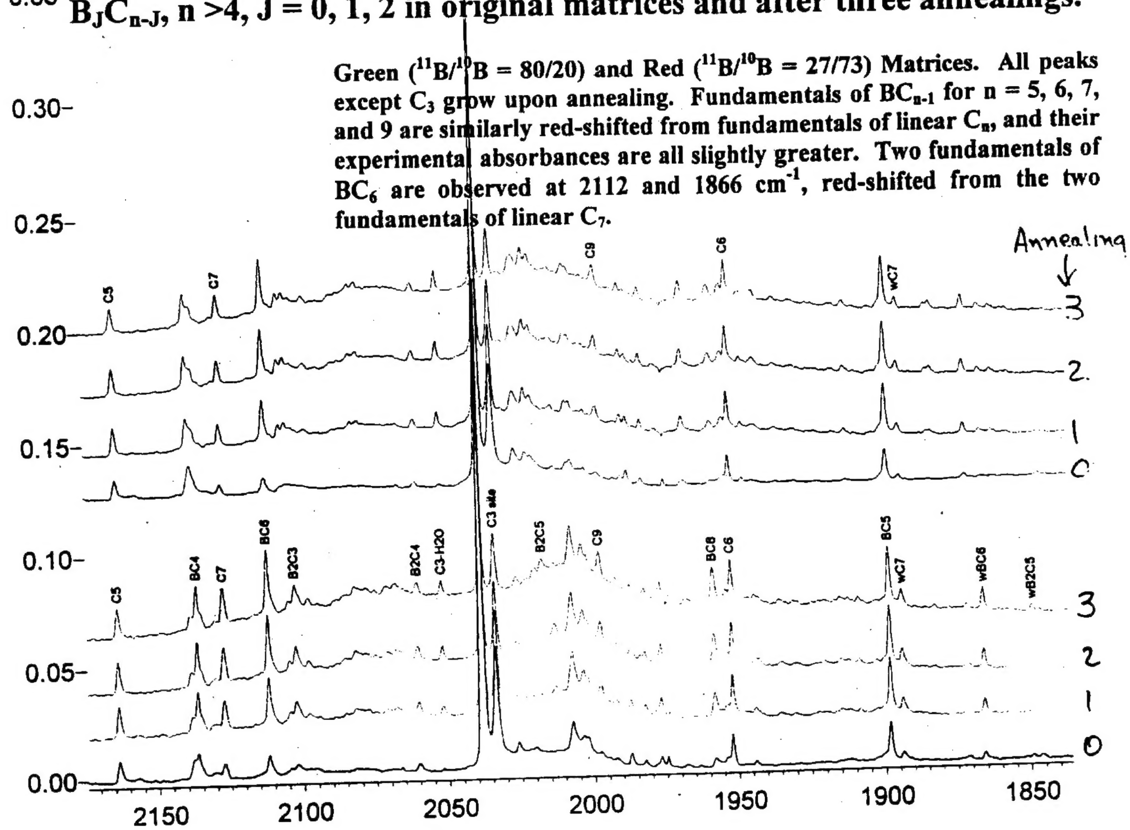
Green Matrix	$^{11}B/^{10}B = 80/20$	enhanced $^{11}B_JC_{n-J}$
Red Matrix	$^{11}B/^{10}B = 27/73$	enhanced $^{10}B_JC_{n-J}$



Survey spectra showing BC_2, B_2C, C_4, BC_3, B_2C_2

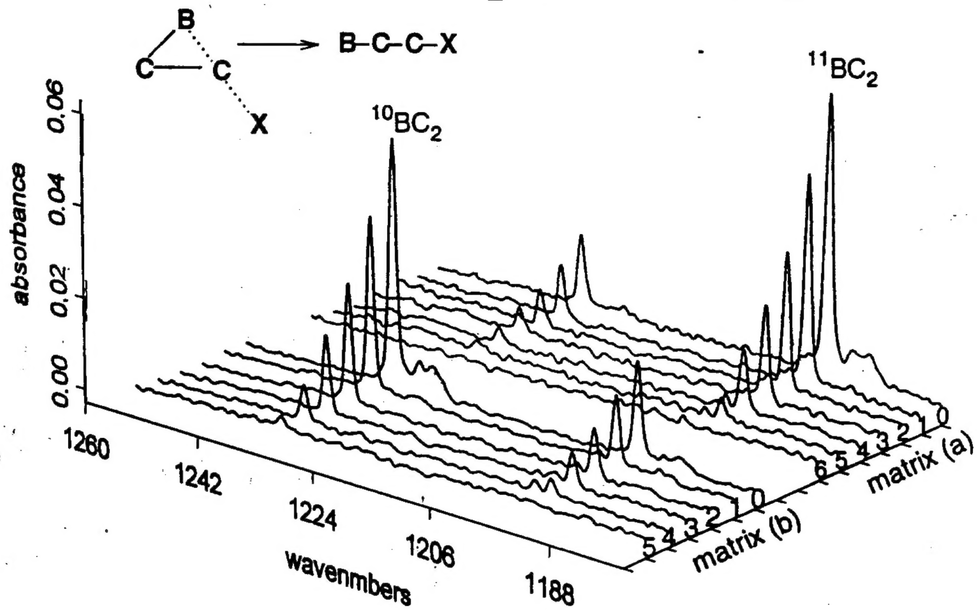
Doublet peaks belonging to $^{10}BC_{n-1}$ and $^{11}BC_{n-1}$ and triplets belonging to $^{10}B_2C_{n-2}$, $^{10,11}B_2C_{n-2}$, and $^{11}B_2C_{n-2}$ are seen with inverted intensity ratios. Note red shift of BC_3 from C_4. BC, B_3, and B_3C were not observed.

Survey spectra of precision matched matrices showing larger clusters B_JC_{n-J}, n >4, J = 0, 1, 2 in original matrices and after three annealings.



Green ($^{11}B/^{10}B$ = 80/20) and Red ($^{11}B/^{10}B$ = 27/73) Matrices. All peaks except C_3 grow upon annealing. Fundamentals of BC_{n-1} for n = 5, 6, 7, and 9 are similarly red-shifted from fundamentals of linear C_n, and their experimental absorbances are all slightly greater. Two fundamentals of BC_6 are observed at 2112 and 1866 cm^{-1}, red-shifted from the two fundamentals of linear C_7.

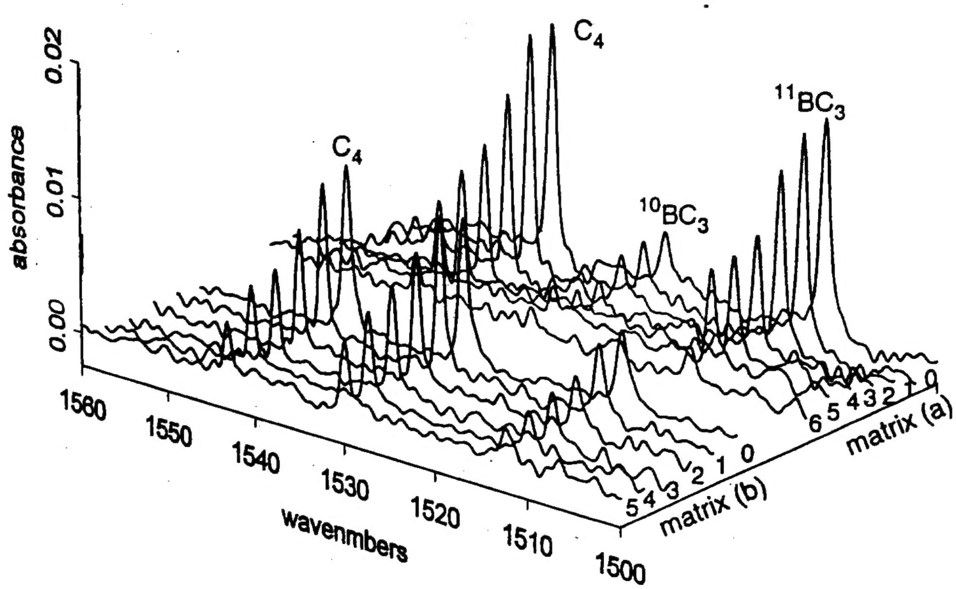
Disappearance of BC_2 upon annealing



BC2rg3D Mar. 8, 2000 9:10:18 AM

Disappearance of BC_3 and C_4 upon annealing

B-C-C-C + X = B-C-C-C-X



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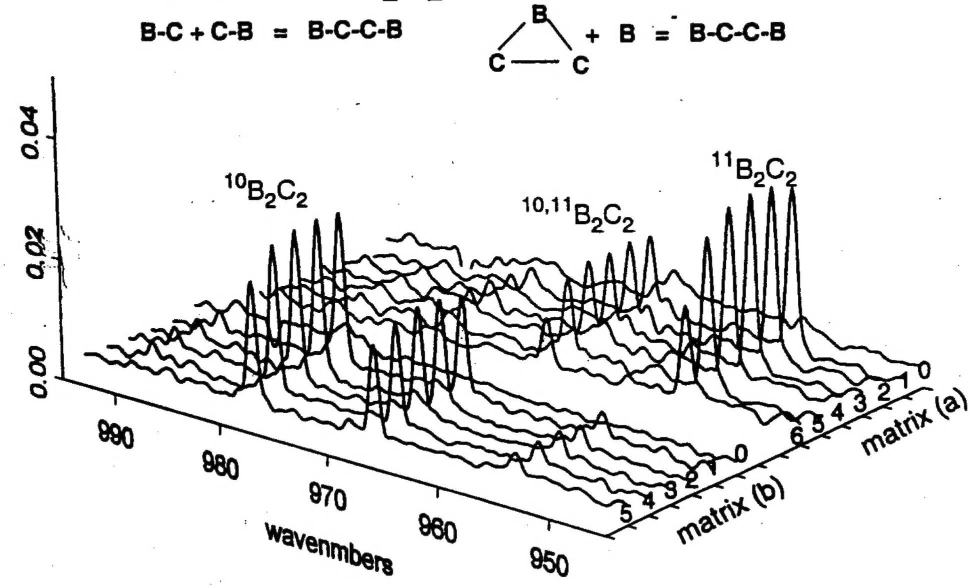
Growth of B_2C_2 upon annealing



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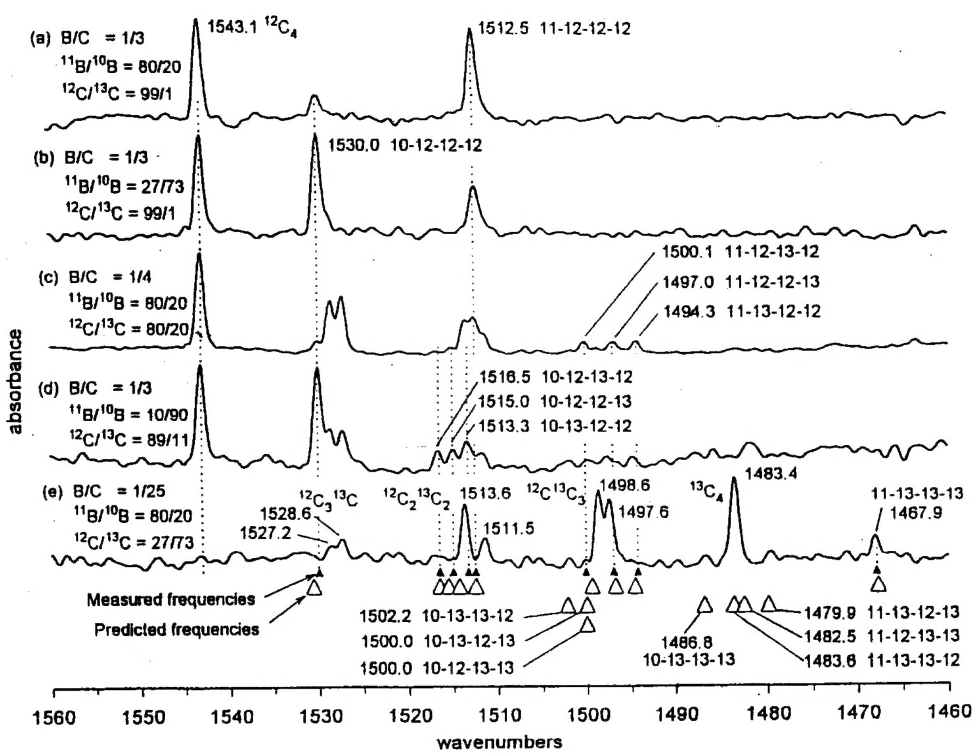
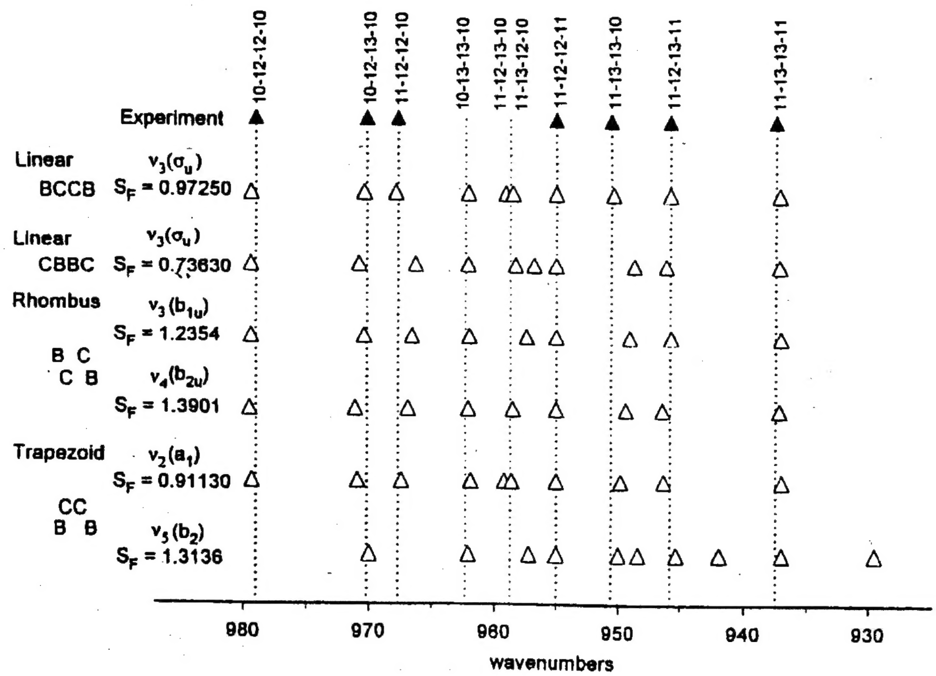
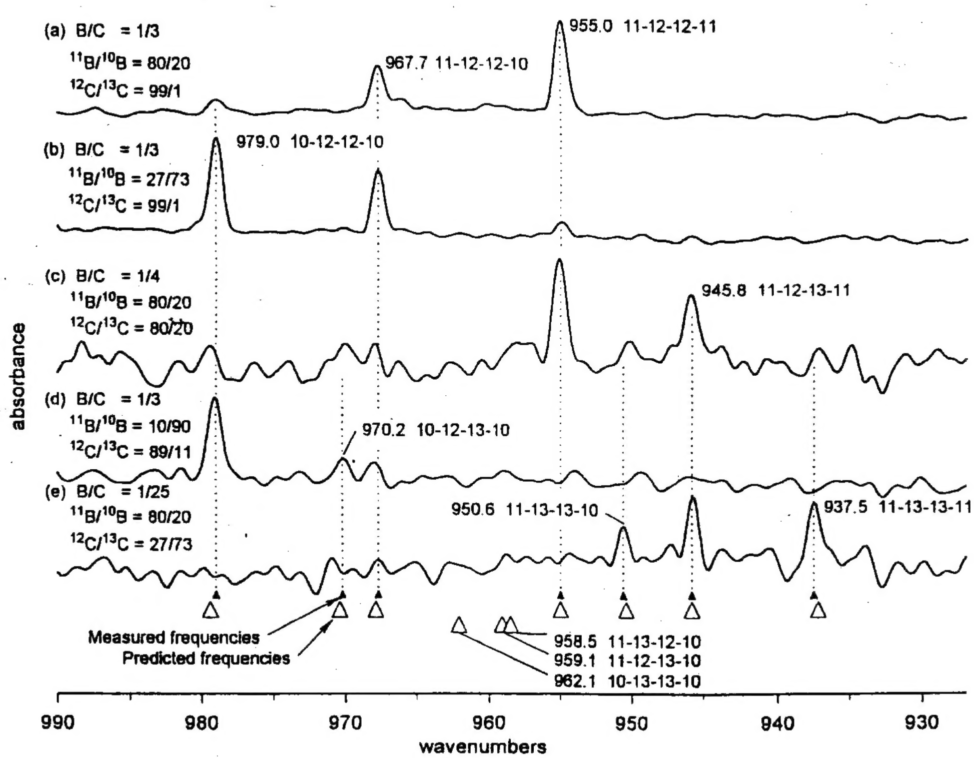
Identification of 9 of the 16 isotopomers of linear BCCC in 5 matrices.



Four minimum energy geometries of B_2C_2 produce similar isotopomer fingerprints. Scale factor (S_F = measured frequency/theoretical frequency) of linear BCCB = 0.97250.



Identification of 7 isotopomers of the 10 isotopomers of BCCB in 5 matrices.

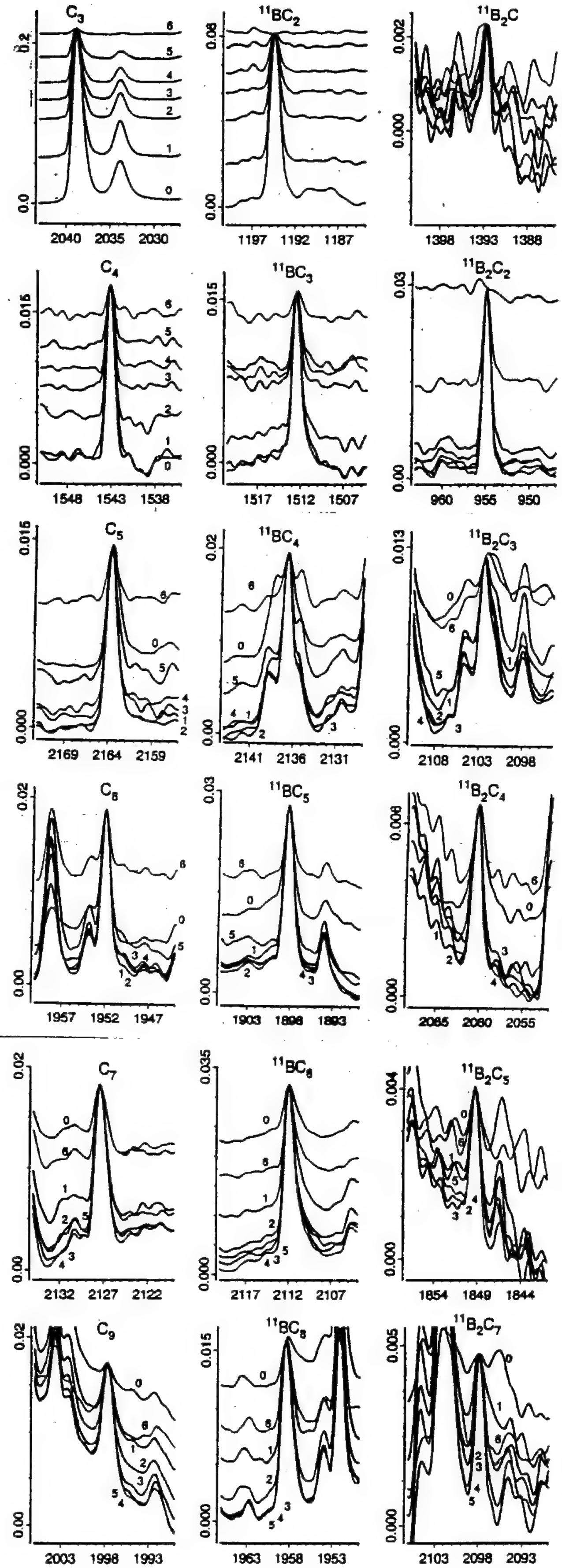


B_JC_{n-J}

Annealing Study

Peak by Peak

Detail



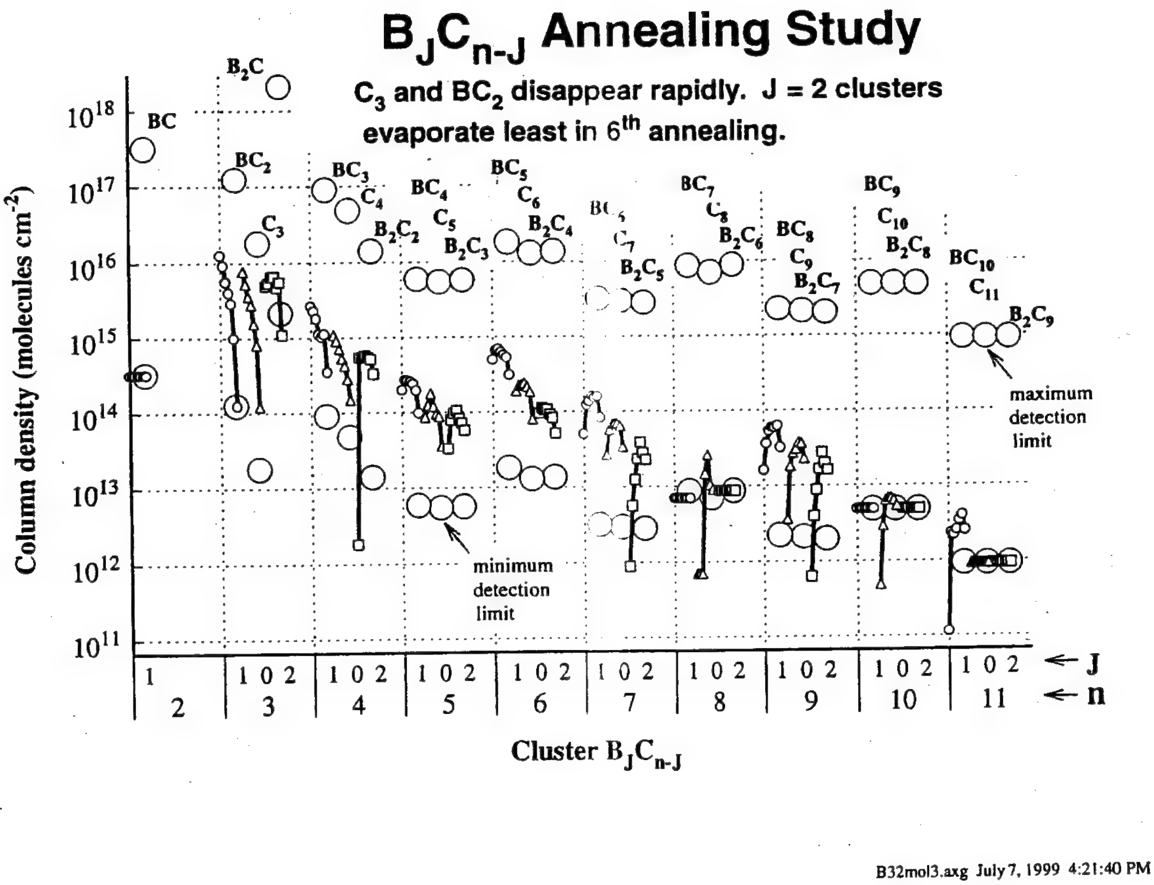
In first annealing C_4 and BC_3 remain constant and B_2C_2 grows from undetectable to S/N ~ 100. B_2C_2 seems inert.

All pentamers grow in first annealing. B_2C_3 grows most; C_5 and BC_4 evaporate most in 5th annealing.

Hexamers with boron grow most; evaporation of C_6 in 6th annealing is greatest.

In 5th annealing, J = 0 evaporates more than J=1, and J = 1 evaporates more than J = 2. A boron rich layer appears to be capped by a carbon rich layer.

In 6th annealing, where almost half the matrix sublimed, the J = 2 clusters evaporate the least. A boron rich layer appears to be capped by a carbon rich layer.



Results and Discussion

Linear C_3, cyclic BC_2, and cyclic B_2C, constituted about 80% of the total observable boron and carbon in the initially deposited matrix, but B_3 was not observed. If B_3 were present, its concentration fell below the detection limit of the system. The measured trimer distribution in the initially formed matrices was $\rho(C_3) : \rho(BC_2) : \rho(B_2C) : \rho(B_3) \sim 1 : 1.5 : 0.5 : < 0.05$ (upper limit).

Statistical substitution of J boron atoms into an n-atom carbon cluster produces a distribution given by $\rho(B_JC_{n-J})/ \rho(C_n) = [\{n(n-1)\ldots(n-J+1)\}/J!]\ [B/C]^J$. With the experimental B/C ~ 1/3, the statistical trimer distribution is

$$\rho(C_3) : \rho(BC_2) : \rho(B_2C) : \rho(B_3) \sim 1 : 1 : 0.33 : 0.03.$$

Agreement between distributions implies trimers form by random condensation of well-mixed atoms, uninfluenced by the relative energies of the trimers, the energies of their precursors, or preferential kinetics pathways that could otherwise distort the statistics.

Linear C_3 and cyclic BC_2, disappeared entirely when the matrices were repeatedly annealed to temperatures between 25 K and 35 K, but cyclic B_2C was inert.

Linear C_4 and BC_3 (BCCC) disappeared more slowly, and linear B_2C_2 (BCCB) grew to ~ 95% of its final value during the first annealing. Once formed, B_2C_2, like B_2C, was also inert to further reaction.

The sources of B_2C_2 are from condensation of atom plus trimer ($B + BC_2$ but not $C + B_2C$) or dimer + dimer ($BC + BC$ but not $B_2 + C_2$). Although BC was not observed, the upper limit of $\rho(BC)$ is larger than $\rho(B_2C_2)$ so that BC cannot be ruled out as a source of B_2C_2.

The growth of B_2C_2 is conclusive evidence of the presence of BC and/or B in the originally deposited matrix in an amount at least as great as the growth of B_2C_2.

Linear C_5, BC_4 (BCCCC) and B_2C_3 (BCCCB)] and larger linear clusters (B_JC_{n-J}, $5 < n < 11$, $J = 0, 1, 2$), all grew upon annealing.

The sources of B_2C_3 are dimer + trimer ($BC + BC_2$ but not $B_2 + C_3$) and atom + tetramer ($B + BC_3$ but not $C + B_2C_2$).

Since $\rho(BC_2) \sim 5\rho(BC_3)$ in the initially deposited matrix, the $BC + BC_2$ source is dominant. Growth of B_2C_3 conclusively establishes the presence of BC in the matrix in an amount at least as great as the amount by which B_2C_3 grows.

Growth of BC_4 occurs primarily by $BC + C_3$ rather than $B + C_4$ or $C + BC_3$ because $\rho(C_3) \sim 10\rho(C_4)$ and $\rho(C_3) \sim 2\rho(BC_3)$. Growth of C_5 occurs by $C + C_4$ and $C_2 + C_3$, which establishes the presence of C and/or C_2 in the original matrix in an amount at least as great as C_5 growth.

Disappearance of triangular BC_2 requires breaking of one of its B-C bonds when one of its carbon atoms is attacked. The major reorganization of electronic energy involved in opening the ring appears to occur with little (< ~3 kcal mol^{-1}) or no energy barrier, which makes this small molecule a candidate for an interesting *ab-initio* study of unusual reactivity at low temperature.

Conclusions

Annealing kinetics of disappearance of C_3 and BC_2, and of appearance of B_2C, C_4, BC_3 B_2C_2, C_5, BC_4, and B_2C_3 unequivocally establishes the presence of atoms and dimers in the originally deposited matrix.

~ 80% or more of the initially deposited HEDM existed as atoms, dimers and trimers.

Molecules with two boron atoms are immune from radical attack and condensation during annealing.

Future Work

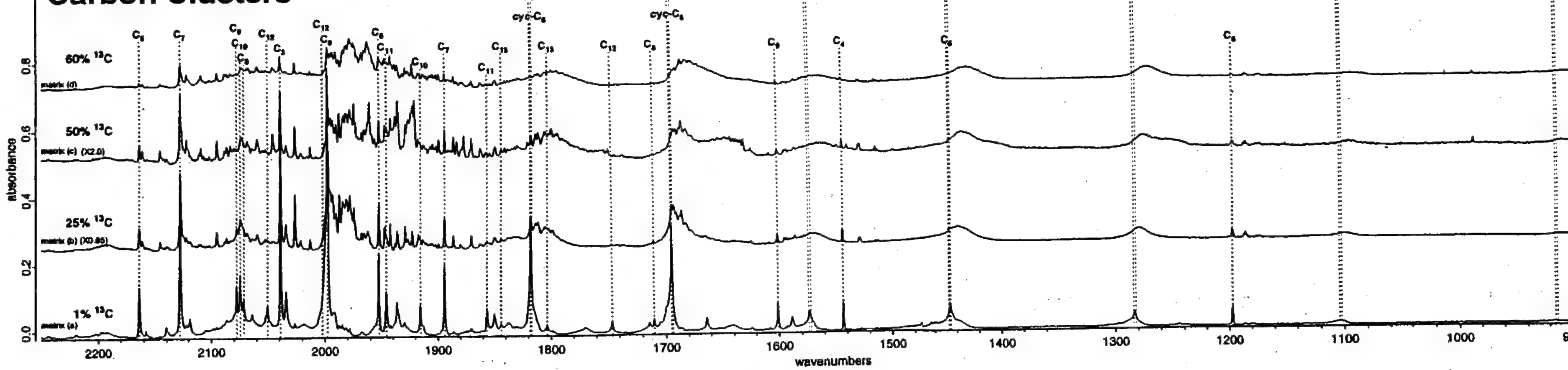
Continued development of source for production of higher flux beam of nearly pure boron atoms.

Map of "islands of stability" of pure boron HEDM; B_2 or B_3 may be the ultimate sink for atoms in the low temperature HEDM environment.

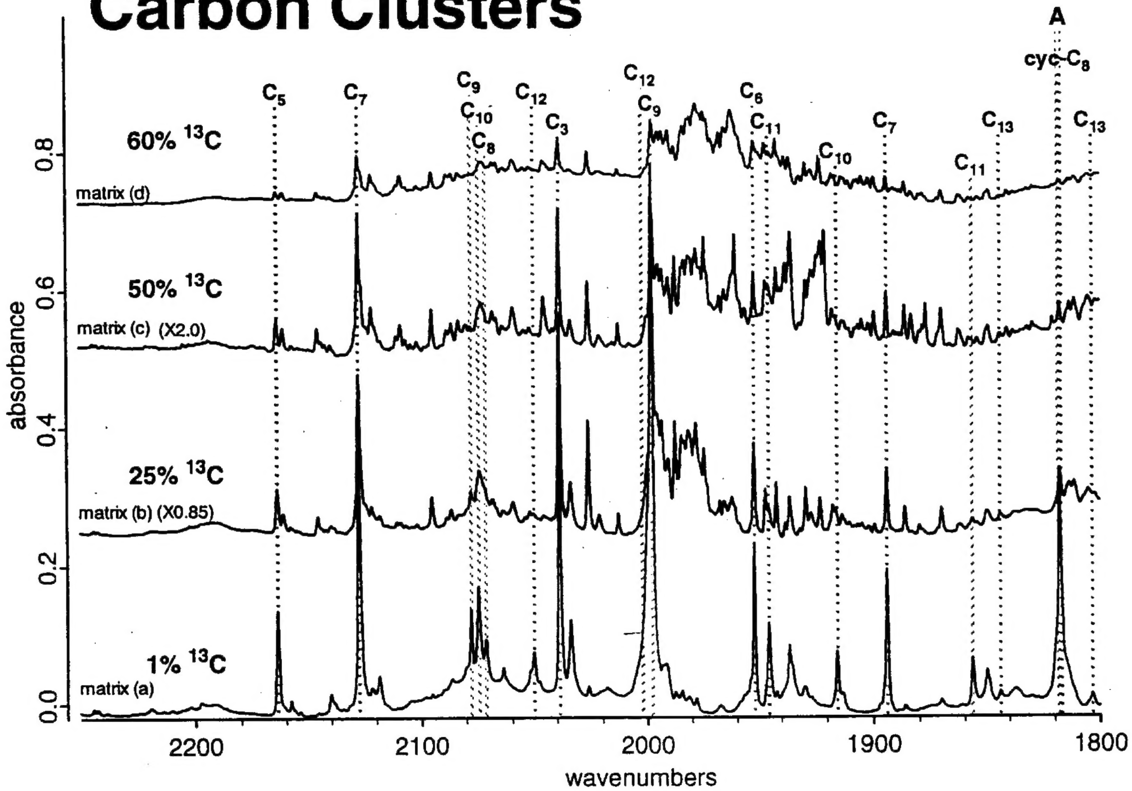
Determine reactivity of boron atoms with hydrogen during co-deposition.

Develop rapid condensation methodology to prevent reaction of B with H_2.

Carbon Clusters



Carbon Clusters



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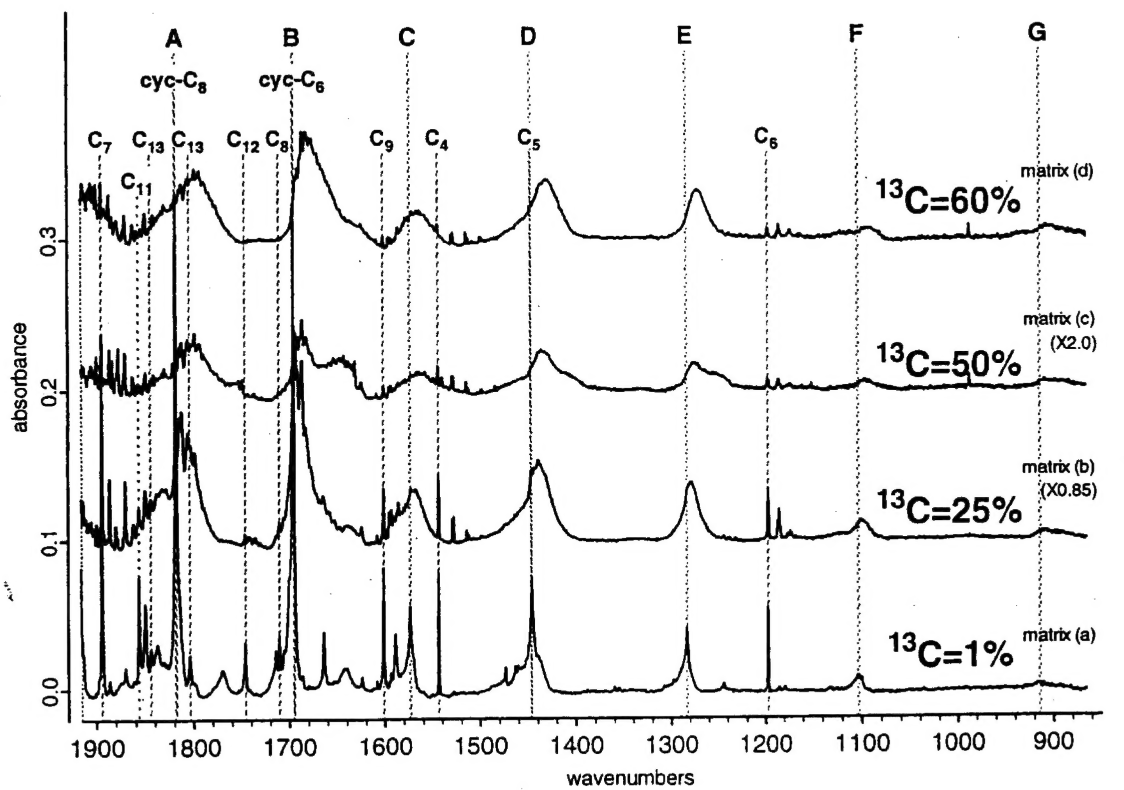
Carbon Clusters



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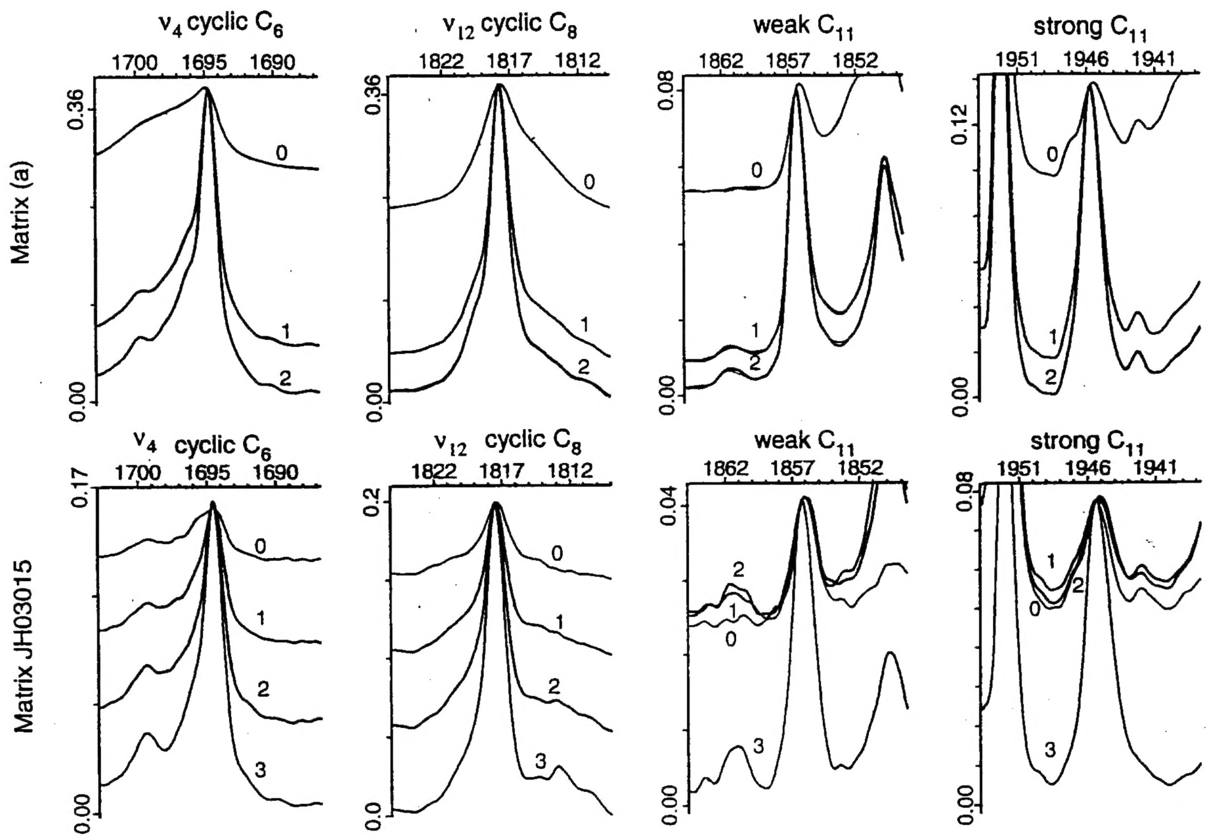
Growth upon annealing - cC_6 and cC_8 - two fundamentals of C_{11}



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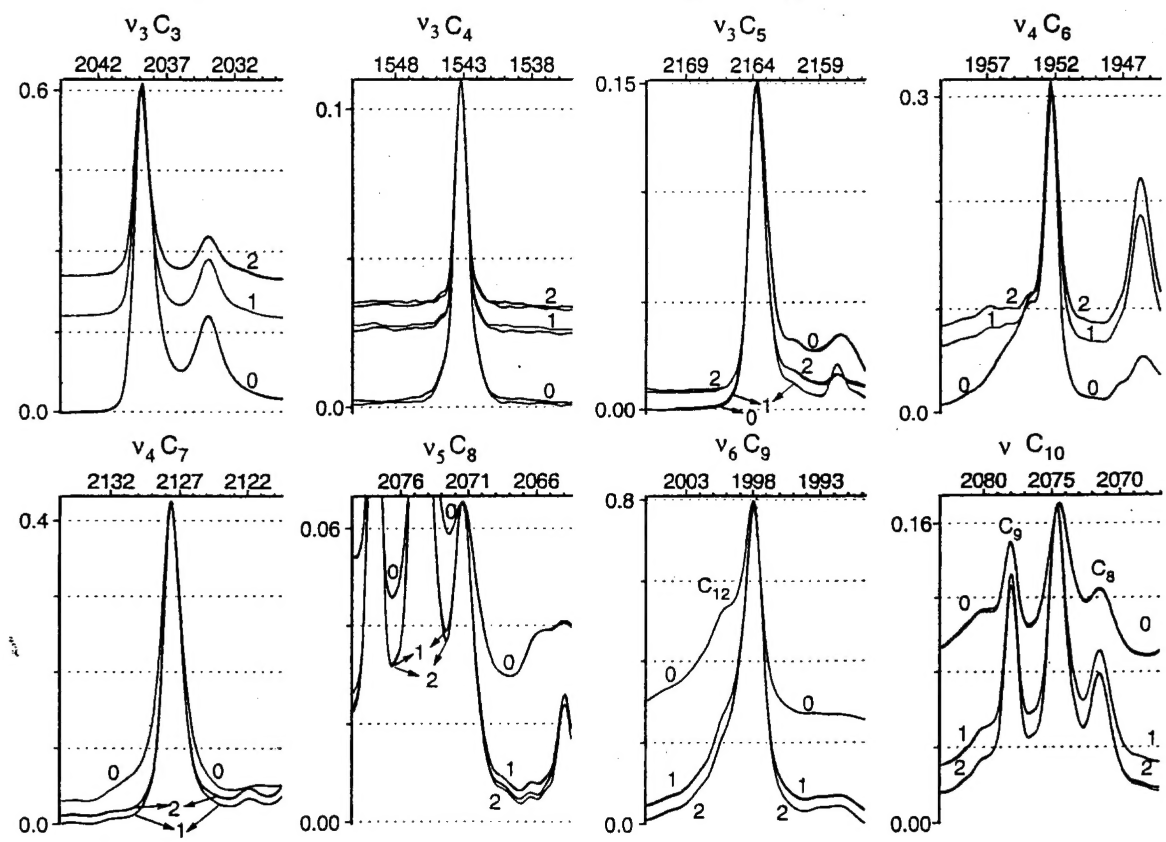
Carbon Matrix (a) - Linear C_3 to C_{10} Clusters



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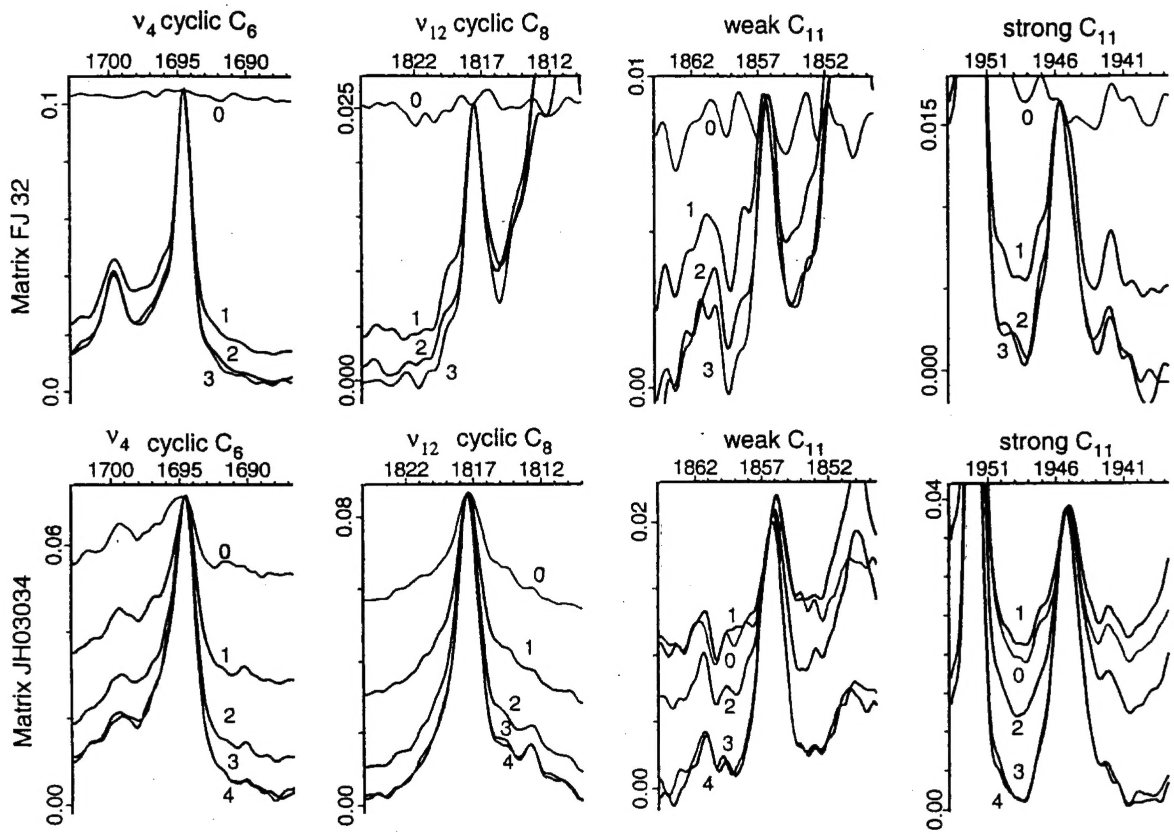

Carbon Matrix FJ 32, JA03034

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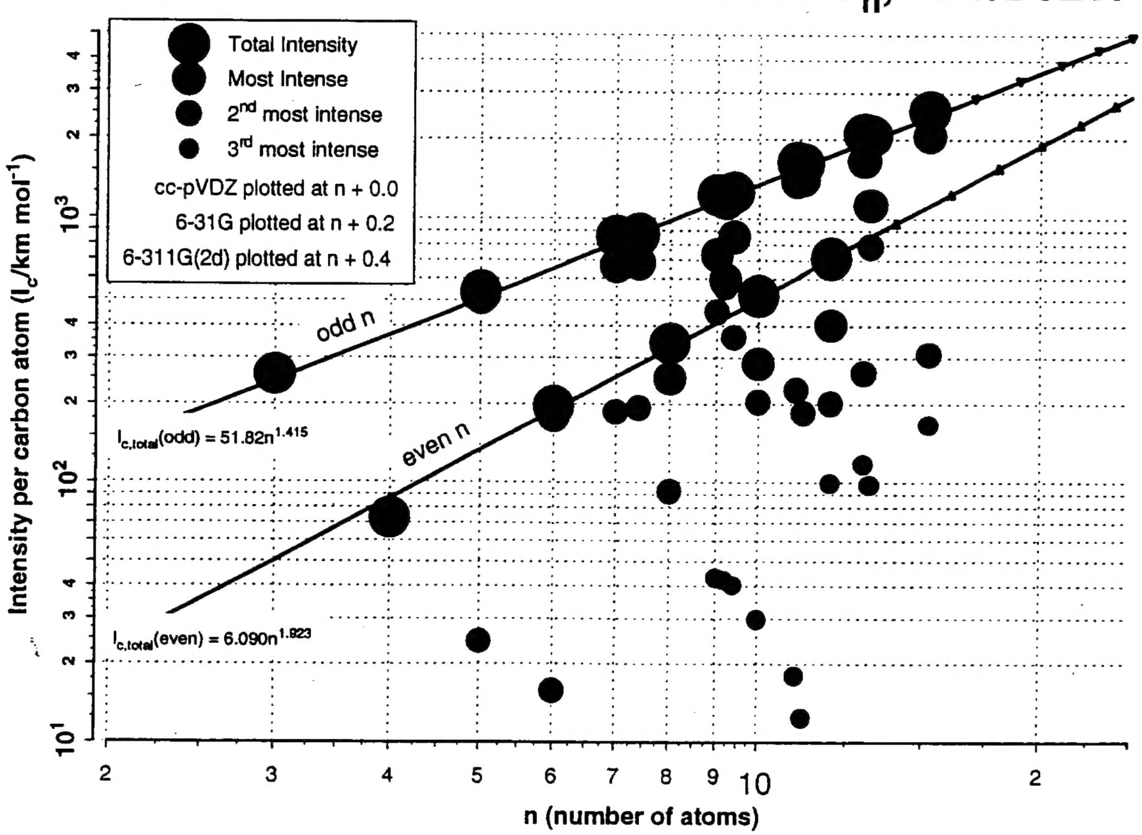
Theoretical Infrared Intensities of Linear C_n, DFT/B3LYP



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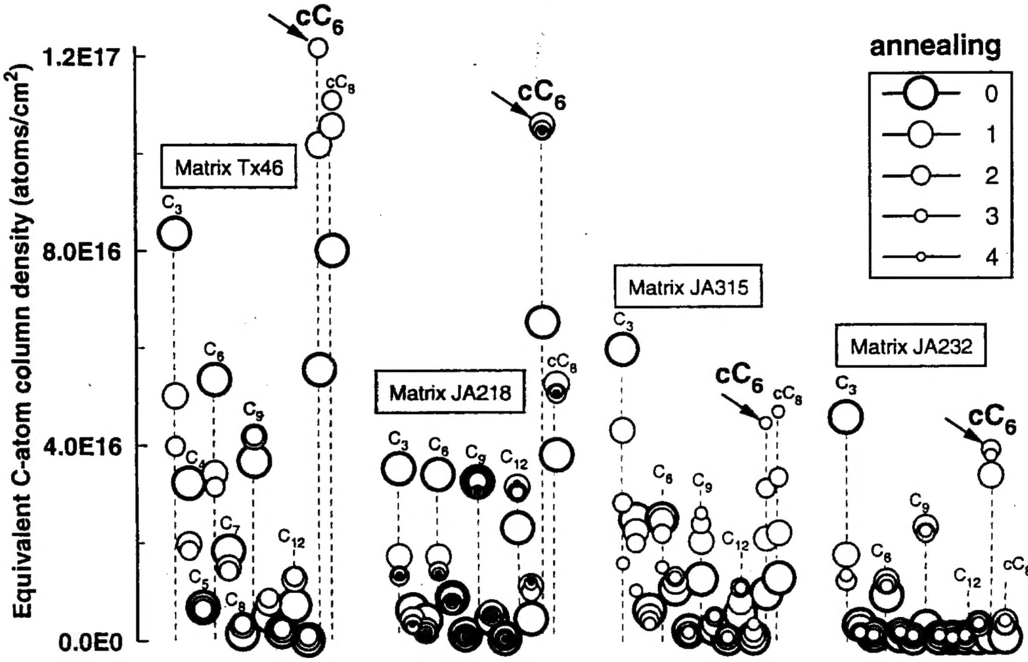
Carbon cluster distributions



Most of the carbon condenses to cC_6 and cC_8 in all matrices

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Conclusions from Carbon HEDM Research

Quantitative analysis - Establishes HEDM density, distribution of carbon clusters, tracking of growth and decay of carbon clusters, carbon bookkeeping - quantification of "invisible carbon", C-atom and C_2.

Highest density matrix (equivalent C-atom density ~ 1 mole percent in argon) contained 40% "invisible" carbon (C, C_2), determined by tracking the growth of the "visible" (measurable) carbon to a constant composition after repeated annealing. Main product of condensation is cyclic C_6.

Yields of cyclic-C_6 are a factor of two larger than the combined yield of all other clusters in the fully condensed, highest density matrices. Cyclic-C_6 is the dominant condensation product.

Substrate must be shielded from oven to prevent condensation during deposition. Higher temperature oven places higher heat load on substrate, which promotes condensation.

Obtained higher density matrices by decreasing argon flux and maintaining oven flux. However, condensation was also increased.

Matrices produced with argon/5% H_2 caused nearly complete loss of C_{n+1} and C_{n+2} relative to C_{n+3}, suggesting that H_2 scavenges C-atoms efficiently during co-deposition.